Dinitrosylcobalt Nitrite: Synthesis and *X*-Ray Crystallographic Structural Studies of a Cobalt Nitrosyl with Bridging Nitrite Groups

By CHARLES E. STROUSE* and BASIL I. SWANSON
(*Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico* 87544)

Summary Treatment of $Co_2(CO)_8$ with an excess of NO in hexane solution results in the formation of $Co(NO)_2NO_2$ which has been characterized by an *X*-ray crystal structure determination and by i.r. studies in the solid state and in solution.

The reaction of $Co_2(CO)_8$ in hexane solution with an excess of NO at room temperature results in the formation of a brown–black, diamagnetic, air and water-sensitive compound.[†] Elemental analysis for this complex gives the empirical formula CoN_3O_4.[‡] The presence of terminal nitrosyl stretching bands in the i.r. spectrum of this very reactive compound suggested its use as a starting material for the preparation of more complicated cobalt nitrosyl complexes. Since no structural data for this compound were available, a study of its solid state and solution structures was undertaken.

Crystals suitable for an *X*-ray investigation were obtained directly from the reaction mixture. Precession photographs show an orthorhombic Laue symmetry (a = 10·48,

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[†] Sabherwal and Burg have recently reported the reaction of $CO_2(CO)_8$ with NO to produce the strong metal base trinitrosylcobalt. $CO(NO)_3$ (*Chem. Comm.*, 1970, 1001). This complex was produced by a vapour phase reaction of $Co_2(CO)_8$ with NO in a sealed tube.

[‡] Elemental analysis of the decomposition products gave results in accordance with the reaction $CoN_3O_4 \xrightarrow{\Delta} CoO + 3NO$. No carbon was found in the sample.

$b = 6{\cdot}94$, $c = 6{\cdot}63$ Å) with systematic absences characteristic of P_{nma} or P_{n2_1a} (non-standard setting of P_{na2_1}). D_m ($2{\cdot}28 \pm 0{\cdot}01$ gcm^{-3}) agrees well with that calculated for four CoN_3O_4 groups per unit cell. Two octants of data were collected on a four-circle Picker automatic diffractometer with Mo-K_α radiation to 45° in 2θ. A total of 654 reflections with intensity above 3σ were obtained and used in the structure determination.

A Patterson function was used to determine the position of the cobalt atom and successive Fourier maps were used to locate the light atoms. The crystal structure (Figure 1) consists of infinite chains of $Co(NO)_2$ moieties linked by nitrite groups with the nitrogen atom of the nitrite co-ordinated to one cobalt atom in the chain and one of the nitrite oxygen atoms co-ordinated to the next cobalt atom. The co-ordination about the cobalt atom is roughly tetrahedral.

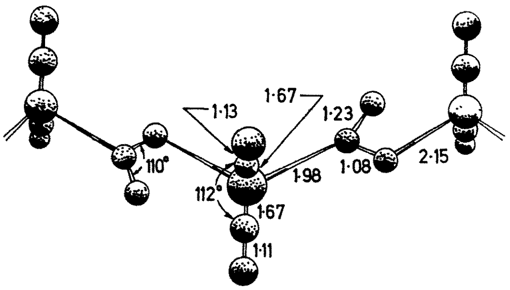

FIGURE 1. *Solid state chain structure of* $Co(NO)_2NO_2$.

Least-squares refinements of the structure were carried out in both the centric and acentric space groups. The structure was refined in the centric space group with the $Co(NO)_2$ fragment on a crystallographic mirror plane and the nitrite moiety disordered about a centre of symmetry at the midpoint of the line joining the co-ordinated nitrogen and oxygen atoms. In the acentric space group all atoms occupy four-fold general positions. The centric model refined to a weighted R_w factor of $3{\cdot}65\%$ while the acentric model gave R_w $2{\cdot}92\%$. The hypothesis that the structure is centric can be rejected at the $0{\cdot}5\%$ level of significance.[1]

All bond distances and angles in the structure are chemically reasonable and comparable to those in similar cobalt complexes with the exception of the bond distance between co-ordinated oxygen and nitrogen atoms in the nitrite anion. This distance, 1·08(3) Å, is shorter than the 1·29—1·31 Å distances observed in nitrite bridges of binuclear cobalt complexes[2,3] and the 1·28 Å distance in $[Ni(en)_2NO_2]BF_4$ (en = ethylenediamine).[4] The significance of this difference is, however, questionable. The large anisotropic thermal parameters for these atoms and presence of a pseudo inversion centre between the two atoms suggest that this short NO distance is inaccurate. The i.r. data reported below support this suggestion.

The chain structure of $Co(NO)_2NO_2$, made up of $Co(NO)_2$ groups bridged by nitrite anions, is similar to that of $Co(NO)_2I$.[5] The nitrite bridges of $Co(NO)_2NO_2$ are of the same type as those found in $[Ni(en)_2NO_2]BF_4$.[4] In both $[Ni(en)_2NO_2]BF_4$ and $Co(NO)_2NO_2$ the metal atoms are nearly in the plane of the nitrite ions to which they are co-ordinated, and the unco-ordinated nitrite oxygen atom is roughly equidistant from the two nearest metal atoms.

I.r. data for solid phase and CCl_4 solutions of $Co(NO)_2NO_2$ and $Co(^{15}N^{18}O)_2{}^{15}N^{18}O_2$ are presented in the Table. The two high frequency bands characteristic of terminal nitrosyl ligands are comparable to those reported for $Co(NO)_2X$ ($X = Cl^-, Br^-, I^-$, and SCN^-),[6] while the two lower frequency bands are similar to N–O stretching modes assigned to the nitrite moiety in binuclear cobalt complexes with bridging nitrite groups.[7,8] These nitrite frequencies are significantly different to those found for nitro- or nitrito-groups.[8,9] The close similarity between solid and solution phase N–O stretching frequencies indicates that the bridging nitrite ions persist in solution. On the basis of this similarity, a dimeric structure is suggested for $Co(NO)_2NO_2$ in solution (Figure 2).

I.r. data in the N–O *stretch region* (*cm*$^{-1}$)

$Co(NO)_2NO_2$		$Co(^{15}N^{18}O)_2{}^{15}N^{18}O_2$	
CCl_4 soln.	Solid	CCl_4 soln.	Solid
1867	1878	1789	1800
1802	1783	1727	1700
1481	1442	1418	*ca.* 1385
1164	1192	1112	1135

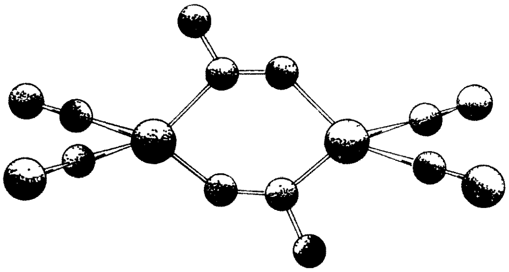

FIGURE 2. *Suggested solution structure of* $Co(NO)_2NO_2$.

Investigations in this laboratory have shown that the reactions of $Co(NO)_2NO_2$ provide new routes to a number of reported cobalt nitrosyl compounds and possibly to new cobalt nitrosyl cluster complexes.

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